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By D. E. Shanks and E. G. Noble

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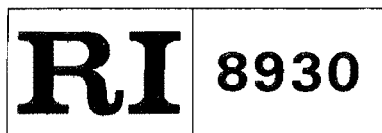
BUREAU OF MINES 75TH ANNIVERSARY

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UNIT OF MEASURE ABBREVIATIONS USED IN THIS REPORT

°C	degree Celsius	mL	milliliter
cm³/min	cubic centimeter per minute	mL/min	milliliter per minute
		mm	millimeter
g	gram		
		pct	weight-percent
h	hour		
		psig	pound (force) per square inch, gauge
hp	horsepower		
in	inch	rpm	revolution per minute
L	liter	sp gr	specific gravity
m	meter		

HYDROGEN CHLORIDE SPARGING CRYSTALLIZATION OF THE CHLORIDE SALTS OF COBALT, MANGANESE, AND NICKEL

By D. E. Shanks[1] and E. G. Noble[2]

ABSTRACT

The Bureau of Mines investigated the effects of HCl concentration and solution temperature on the solubility and crystal form of the chlorides of Co, Mn, and Ni when sparged with HCl gas at temperatures of 20°, 40°, and 60° C. Increasing HCl concentration in solution caused the chlorides of Co, Mn, and Ni to crystallize (salt out) because of the common ion effect. The salting-out crystallization was most effective for $NiCl_2$, which had a solubility of 0.7 pct at 20° C and maximum HCl concentration. $CoCl_2$ salted out to a minimum solubility of 9.4 pct at 20° C and 22 pct HCl concentration and increased in solubility at greater HCl concentrations because of the formation of chloride complexes. $MnCl_2$ was intermediate in behavior. The effect of temperature on solubility was greatest for $CoCl_2$ and least for $NiCl_2$, 15 and 7 pct change, respectively, over the temperature range of 20° to 60° C.

The salted-out chlorides of cobalt and nickel formed the hexahydrates and those of manganese formed the tetrahydrate in saturated metal chloride solutions at 20° C and low concentrations of HCl. Increasing the temperature or the HCl concentration caused a loss in waters of hydration. At 60° C, the salted-out crystals of $NiCl_2$ formed the tetrahydrate in HCl concentrations up to 18 pct and the dihydrate at higher concentrations, while cobalt and manganese chlorides formed the dihydrates, even in water.

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INTRODUCTION

Stricter control of effluents and declining ore grades have caused an increase in interest in hydrometallurgical processing. Much of the new technology in hydrometallurgical processing makes use of acid chloride systems. Chloride processing for recovery of Mg, K, and Li from seawater and brines has been practiced for many years. Most of the chlorides are highly soluble in aqueous solution, but many can be removed from solution as a consequence of dramatic decreases in solubility resulting from the common ion effect caused by increasing the chloride ion activity.

Practical use of the sensitivity of chloride salt solubility to changes in HCl concentration can significantly improve the efficiency of chloride hydrometallurgical processes. For example, in the HCl process for producing alumina from clay, a pure, crystalline $AlCl_3 \cdot 6H_2O$ product is recovered from contaminated pregnant liquors by the decrease in solubility caused by addition of HCl gas.

The goal of this study is to stimulate interest in and expand the data base for sparging crystallization of chlorides of metals having strategic or critical economic importance by investigating the effects of HCl gas concentration and solution temperature on the solubility, chemical composition, and physical characteristics of the salted-out metal chloride crystals.

Limited data are available on the solubility and solid phases formed during the salting-out crystallization of chloride salts with HCl. The data were gathered in long-term equilibrium tests using closed containers and predetermined amounts of constituents. Publications published prior to 1956-57 were summarized in Linke-Seidell (1).[3] Only four references, the $CoCl_2$-HCl-H_2O system at 0° C by Engel (2), the $CoCl_2$-HCl-H_2O system at 25° C by Bassett and Croucher (3), the $CoCl_2$-HCl-H_2O and $NiCl_2$-HCl-H_2O systems at 0° C by Foote (4), and the $NiCl_2$-HCl-H_2O systems at 20° C and 80° C by Babaeva and Archakova (5), are cited. A recent paper by Balarew, Spassow, and Simeonawa (6) covered the solubilities and crystal hydrate salts of the $NiCl_2$-HCl-H_2O system at 25° C and the $MnCl_2$-HCl-H_2O system at 25°, 40°, and 50° C. Salting-out crystallization occurred in all three systems; $CoCl_2$ was initially the least soluble and $MnCl_2$ was the most soluble. This relationship changed at high HCl concentrations, where $CoCl_2$ formed chloride complexes and became considerably more soluble, while $NiCl_2$ continued to salt out and became much less soluble. There was an increase in solubility and a decrease in hydration with increasing temperature.

Earlier sparging crystallization work by the Bureau of Mines to purify $AlCl_3$ (7) showed that the solubility curves matched those obtained by the equilibrium method used by Malquori (8), Seidell and Fischer (9), and Brown, Daut, Mrazek, and Gokcen (10). If this relationship holds for other chloride salts, the data base on chloride salt behavior in aqueous HCl could be rapidly and easily expanded by carrying out HCl sparging experiments. Data collected would also be more relevant to metallurgical applications than data collected from long-term equilibration tests because of the more realistic time span.

MATERIALS AND EQUIPMENT

Sparging was performed in a 3-L water-jacketed borosilicate glass resin reaction kettle with a four-port lid fitted with standard taper joints (fig. 1). Temperature was controlled by a refrigerated circulator bath (-15° to 100° C,

±0.02° C control accuracy) connected by rubber tubing to the sparging tank water

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[3]Underlined numbers in parentheses refer to items in the list of references preceding the appendix.
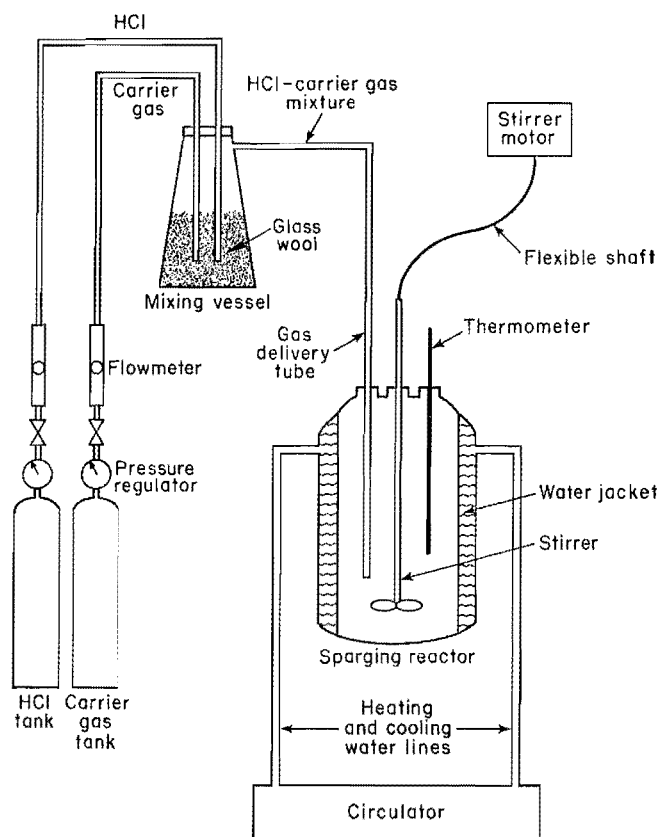
FIGURE 1. - Sparging apparatus.

diameter, and 45° pitch) connected by a flexible shaft assembly to a variable-speed 1/40-hp electric motor capable of 0- to 6,000-rpm armature shaft speed. A Teflon[4] standard taper inlet adapter with slightly oversized 1/4-in hole was used as a centering device and bushing for the stirrer. The bushing was not made gas tight because the carrier gas had to be removed from the system.

Each experiment started with a saturated solution of the metal chloride. The solutions were prepared by heating 1 to 2 L of water to slightly greater than the desired temperature, slowly stirring in an excess of the chloride (Baker Analyzed Reagent grade) until excess solids remained for at least 24 h after the last addition, and cooling to the desired temperature. Reagents used to make saturated solutions included crystals of manganous chloride, $MnCl_2 \cdot 4H_2O$; cobalt chloride, $CoCl_2 \cdot 6H_2O$; and nickelous chloride, $NiCl_2 \cdot 6H_2O$. The sparging gas was Matheson technical-grade hydrogen chloride, >99 pct HCl. Reagents used for analytical purposes were standardized 0.1$\underline{N}$ HCl and carbonate-free NaOH, and ACS reagent-grade silver nitrate.

jacket. Temperature was monitored with mercury thermometers marked in 0.1° C increments.

Sparging and carrier gases were delivered through pressure regulators and flowmeters to a mixing chamber and through a glass sparging tube located just above the propeller located in the sparger vessel. The HCl gas was controlled by a regulator containing a check valve to prevent the return flow of gas into the tank. The HCl and carrier gas flows were measured with rotameters containing glass floats designed to measure flows of 100 to 2,440 cm^3/min and 20 to 386 cm^3/min, respectively. The mixing chamber consisted of a 1-L filter flask filled with glass wool. The contents of the sparger vessel were mixed with a three-bladed, steel-reinforced, linear polyethylene stirrer (18-in length, 1/4-in shaft diameter, 1-3/4-in propeller

Chloride crystals were filtered through 3-L coarse-porosity fritted glass Buchner funnels. Crystal-free samples of solution were removed from the crystallizer through 12-mm-diam coarse-porosity fritted glass cylindrical gas dispersion tubes. Hydrogen and total chloride ion concentrations were determined with an automatic titrating apparatus with motor-driven burette and magnetic stirrer, utilizing a standard pH electrode for hydrogen ion titrations and a chloride ion-specific electrode for chloride titrations. A sleeve-type double-junction calomel internal reference electrode with salt bridge filling solution of sodium acetate-sodium nitrate in water was used.

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[4]Reference to specific products does not imply endorsement by the Bureau of Mines.

Cobalt, manganese, and nickel concentrations were determined by atomic absorption spectroscopy and by chloride titrations after allowing for the chloride contribution from HCl. The cation concentrations were confirmed by a gravimetric technique in which measured volumes of the hydrated chlorides were dried in air at 200° C for at least 12 h and weighed to determine anhydrous chloride content.

PROCEDURE

Saturated chloride solutions were maintained at temperatures of 20°, 40°, or 60° C, and sparged with a mixture of HCl and carrier gases until saturated with HCl. The HCl passing through the Matheson 603 flow meter was adjusted to a flow rate of 36 units in a 150-unit scale, which equated to a flow rate of 850 mL/min. The carrier gas, air or nitrogen, was regulated at 10 psig and delivered at 100 units on the Matheson 602 flow meter, which corresponded to a flow rate of 200 mL/min. The carrier gas was added because experience with $AlCl_3$ crystallization showed that larger, purer crystals were produced, fewer problems were encountered with sparger tip plugging, and solution aspiration was eliminated. Stirrer speed was not measured, but was continuously adjusted to the minimum speed that would keep the solids in suspension. The 850-mL/min HCl flow rate was the fastest flow that could be utilized without exceeding the cooling capacity of the circulator (HCl hydration is very exothermic) and gave a reasonable sampling frequency. The chloride salt slurry was sampled prior to sparging and then hourly until the conclusion of the experiment. Approximately 5-mL samples were drawn from the slurry through a fritted glass gas dispersion tube to insure that no solids were removed. The solution was added to a volumetric flask approximately half full of a weighed amount of water. The volumetric flask was weighed after the sample was added and again after the flask was filled to the 100-mL mark. This procedure minimized loss of HCl and allowed for calculation of the weight of the sample and density of the diluted sample. The specific gravity was determined directly on the 20° C samples with a Mettler-Paar DMA 35 density meter. For measurement of specific gravity at temperatures outside the 10° to 30° C range of the instrument,

a 5-mL sample of the solutions was weighed. Glassware for handling undiluted samples was heated to greater than operating temperature to prevent precipitation. An approximately 5-mL slurry sample was collected with a ladle. The solids were partially dried by blotting on glass fiber filter paper, weighed, dissolved in water, and made up to volume in a 100-mL volumetric flask.

The three samples were used to determine HCl concentration in solutions and wet residues, metal chloride concentration in solutions and wet residues, and solution densities. To improve sampling precision, 1-mL aliquots were withdrawn from the volumetric flasks and weighed, and the weight was divided by the density of the solution. The HCl concentration was determined by diluting a 1-mL aliquot to 50 mL with water and titrating with standardized 0.1000N NaOH. The automatic titrator determined the end point as the inflection point of the titration curve and printed out the volume of titrant consumed in reaching the endpoint. HCl concentration was calculated from the equation

$$R_1 = E_1 \times C_1 \times C_2/C_3 \times C_4,$$

where R_1 = concentration of HCl, pct,

E_1 = NaOH volume, mL,

C_1 = 364.6 = meq wt HCl × volumetric flask volume × conversion factor wt fraction to wt pct,

C_2 = 0.1000 = NaOH $\underline{N}$,

C_3 = volume of aliquot titrated, mL,

and C_4 = weight of sample, g.

Metal chloride concentration was determined by titrating a 1-mL aliquot with standardized 0.100N silver nitrate ($AgNO_3$) and a chloride-specific ion electrode. The endpoint volume was converted to metal chloride concentration by the formula

$$R_2 = \left(\left(\frac{E_2 \times C_6}{C_7}\right) - R_3\right)(C_5/C_4),$$

where R_2 = metal chloride concentration, pct,

E_2 = $AgNO_3$ volume, mL,

C_5 = 649.2 for $CoCl_2$, 629.2 for $MnCl_2$, and 648.1 for $NiCl_2$,

C_6 = $AgNO_3$ concentration, N,

C_7 = volume of aliquot titrated with $AgNO_3$, mL,

R_3 = correction for chloride contributed by HCl = E_1 × C_2/C_3,

E_1 = NaOH volume, mL,

C_2 = 0.1000,

C_3 = volume of aliquot titrated with NaOH, mL,

and C_4 = weight of sample, g.

Metal chloride was checked by a gravimetric technique in which 25-mL aliquots were dried under heat lamps, heated to 200° C in a muffle furnace, cooled in a vacuum desiccator, and weighed as the anhydrous chloride. Atomic absorption spectroscopy on low-metal-chloride concentrations was used to supplement the gravimetric results.

The experiments were terminated when HCl sparging ceased to influence the HCl and chloride salt concentrations. The slurries were filtered through fritted glass to separate solids from solution. The solids were examined microscopically to determine their morphology. The wet-residue and solution compositions were plotted on triangular coordinate paper, and tielines were constructed to determine crystal composition by Schreinemakers' wet-residue method (11).

PRECISION AND ACCURACY

The usual problems of evaluating the analytical precision and accuracy of the measured parameters were present. A potentially more serious accuracy problem inherent in this research was chemical nonequilibrium. In conventional studies, premeasured quantities of reagents are shaken in closed containers for long periods of time, while maintaining constant temperature. Readings are taken until the systems are in equilibrium. With the sparging technique, concentrations of reagents are constantly changing and HCl can easily escape. Comparison of equilibrium data from previous and current studies indicated that the reaction kinetics are very fast and HCl is not easily lost from solution. This was confimed by measurements made after sparged slurries were allowed to stand overnight without additional sparging. Metal chloride and HCl concentrations changed by less than 0.1 pct. Simultaneous bottle tests of 2 weeks' duration gave almost identical results.

The titration of chlorides and HCl represented the major precision-limiting step in the solubility determinations. In several hundred titrations of 0.1000N HCl with $AgNO_3$ and NaOH to determine chloride and HCl concentrations, average values of 0.0991 ±0.0011N were indicated for $AgNO_3$ and NaOH concentrations of the titrants. This represents an absolute variation of ±1.1 pct for each titration, and since the contribution of chloride from HCl must be subtracted from the total chloride concentration, the two errors are additive and give up to 2.2 pct error. The variation of data points from the smoothed curves was up to ±0.1 pct (a 1.0-pct error on an absolute basis for a sample containing 10 pct HCl and 10 pct

metal chloride) and was the other primary source of error. Some of the ancillary measurements had larger relative errors, but had no bearing on the precision and accuracy of the solubility work. For instance, the estimated precision of HCl flow rate measurements was ±5 pct, but experience gained from $AlCl_3 \cdot 6H_2O$ crystallization showed that HCl flow rate was not an important parameter at flow rates less than 1,300 mL/min. Specific gravity measurements at 40° and 60° C showed considerable scatter and varied as much as ±3 pct; therefore, the values reported for specific gravity in tables A-1 to A-9 (appendix) were determined from smoothed curves. Other sources of error were minor. Originally, pipetting errors of up to 2 pct were noted, but this source of error was decreased by at least an order of magnitude by weighing the samples and dividing by the density to get correspondingly accurate volumes. The volumetric flasks were certified to contain 100±0.08 mL of solution, which calculates to a maximum error of 0.08 pct. Temperatures were measured with thermometers marked in 0.1° C increments and estimable to 0.02° C. Observed temperature variations were within 0.05° C. Each thermometer was calibrated against a set of National Bureau of Standards (NBS) certified thermometers and read within ±0.1° C of the certified temperature in the 20° to 60° C range. Temperature variations of 0.1° C would lead to a maximum metal chloride concentration error of 0.1 pct.

RESULTS AND DISCUSSION

The most important common properties of the three systems were the rapid approach to equilibrium and the maintenance of equilibrium conditions in the HCl environment created by HCl sparging. The kinetics were not studied per se, but rapid attainment of equilibrium was inferred from the close agreement between this study, earlier research by others in which equilibrium was attained, and separate equilibrium studies conducted in this research.

The three compounds evaluated were very soluble in water. Their solubilities were highly temperature dependent over the temperature range investigated and ranged from 34.6 to 52.1 pct. Increasing the HCl concentration by sparging caused a decrease in solubilities of the three metal chlorides due to the common ion effect. The decrease in solubility was most pronounced for $NiCl_2$. A minimum of 0.7 pct $NiCl_2$ at 37.1 pct HCl concentration was obtained. This contrasts to the minimum solubilities of 9.4 pct for $CoCl_2$ and 11.3 pct for $MnCl_2$ at HCl concentrations of 22.0 and 34.0 pct HCl, respectively. The solubility minimums for both $CoCl_2$ and $MnCl_2$ occurred before the solutions were saturated with HCl. This behavior is due to chloride complexation at high HCl concentration and results in increased solubilities of 18.1 pct $CoCl_2$ and 11.9 pct $MnCl_2$ in solutions saturated with HCl.

The slopes of the solubility curves for Co, Mn, and Ni chlorides were almost identical for the initial salting-out portions of the diagrams (figs. 2, 6, and 10). Solubility differences for solutions up to about 20 pct HCl concentration were due to the differences in aqueous solubility at a given temperature. At HCl concentrations greater than 20 pct, solubility differences were due to differences in chloride complex formation. $NiCl_2$ does not form strong chlorocomplexes and its solubility decreases when the HCl concentration is increased, whereas $CoCl_2$ forms strong chlorocomplexes and increases in solubility at greater HCl concentrations. $MnCl_2$ is intermediate in both complexing response and solubility.

Increasing both temperature and HCl concentration decreases the hydration state of the salted-out crystals. Cobalt and nickel chlorides were in equilibrium with hexahydrate salts, and $MnCl_2$ was in equilibrium with tetrahydrate salt at 20° C in water. These chlorides were in

equilibrium with dihydrate salts in concentrated HCl at 60° C. The dehydration to dihydrate crystals was not desirable because the dihydrates formed very small, needlelike crystals that were difficult to filter.

Data for the three systems at the temperature ranges investigated are summarized in tables A-1 to A-9. The information in each table represents a composite of two or three experiments and is discussed in the following sections. From these tabulations, the solubility curves in figures 2, 6, and 10 and the tieline diagrams in figures 3-5, 7-9, and 11-13 were plotted.

COBALT CHLORIDE

$CoCl_2$ concentration and specific gravity as functions of HCl concentration at 20° C are tabulated in table A-1 and plotted in figures 2 and 3. The $CoCl_2$ solubility curve in figure 2 is almost linear with a slope of -1.4 pct $CoCl_2$ per percent HCl up to an HCl concentration of 14 pct. There is a solubility minimum of 9.4 pct at 21 pct HCl, and a rapid increase in solubility to 16.5 pct $CoCl_2$ at 24 pct HCl. This is an invariant point where solid $CoCl_2 \cdot 6H_2O$ and probably $CoCl_2 \cdot 2H_2O$ are in equilibrium with the solution, as evidenced by the change in the intersection of tieline plots in figure 3 and the change in crystal habit from large, red basal tablets to very small, blue-violet, elongated prisms. The tieline data are not clear on the species produced at the break from the hexahydrate. The lower hydrate could be a tetrahydrate or dihydrate, or it could be of the form $HCl \cdot CoCl_2 \cdot 7H_2O$; previously published data (1) show a hexahydrate to dihydrate transition. A secondary minimum of 15.8 pct $CoCl_2$ at 27 pct HCl is followed by a solubility increase to 18.1 pct $CoCl_2$ at HCl saturation, 31.9 pct. Saturation of HCl should be slightly lower at the location of this experiment, owing to the reduced average ambient atmospheric pressure of 642 mm of Hg at an elevation of 1,402 m above mean sea
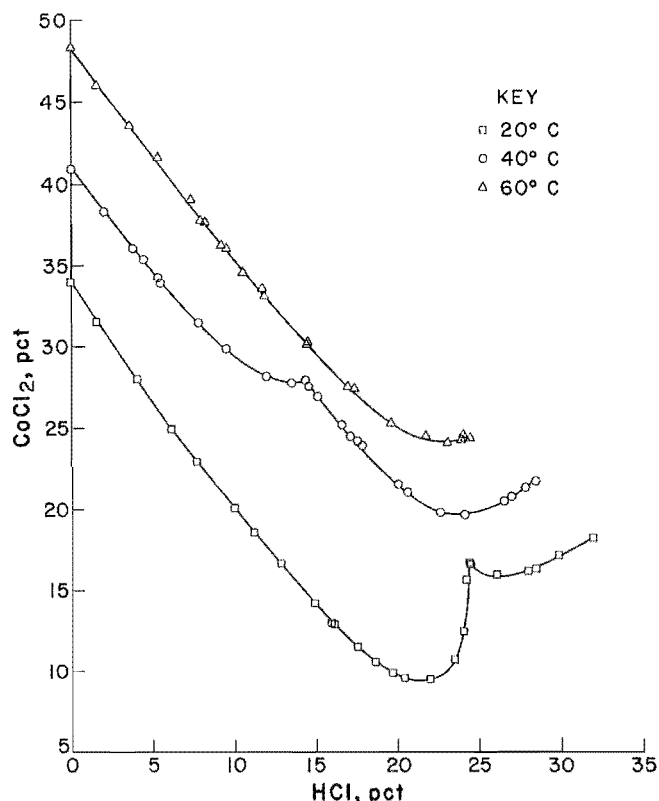
FIGURE 2. - Solubility of $CoCl_2$ as functions of HCl concentration and temperature in the system $CoCl_2$-HCl-H_2O.
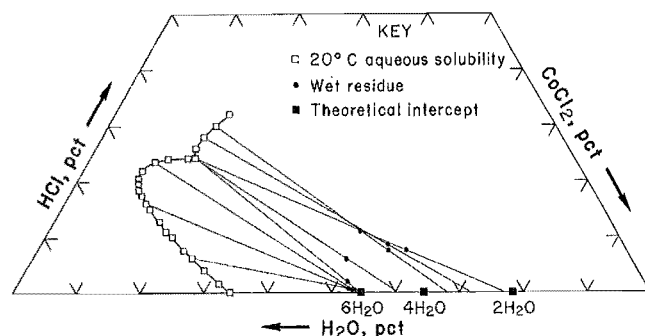
FIGURE 3. - Tieline plot of the data for the $CoCl_2$-HCl-H_2O system at 20°C.

level, as compared with most sea level locations with an average ambient atmospheric pressure of 760 mm Hg.

No previously published values are available for the $CoCl_2$-HCl-H_2O system at 20° C, except the saturation point in water, which is reported as 34.6 pct

by Linke-Seidell (1). This is close to the 33.9-pct solubility determined in this study. The CoCl₂-HCl-H₂O system was studied at 0° C (4) and at 25° C (3). The CoCl₂ solubility curve in this research is similar in shape to the curves of Foote (4) and Bassett and Croucher (3); the point of solid-phase transition from the hexyhydrate to the dihydrate is intermediate in position but closer to the 25° C curve. Linke-Seidell (1) included 0° C data from Engel (2) which are considerably different from Bureau and Foote's research. This discrepancy is probably due to typographic errors either in Engel's original publication or in Linke-Seidell, for when Engel's data are multiplied by 10, they match Foote's data.

CoCl₂ concentration and specific gravity as functions of HCl concentration at 40° C are tabulated in table A-2 and plotted in figures 2 and 4. The CoCl₂ solubility curve for 40° C is almost parallel to the 20° C curve and has the same configuration. The solubility of CoCl₂ in water was 40.9 pct as compared to 41.0 pct in Linke-Seidell. The initial slope was -1.3 pct CoCl₂ per percent HCl. There was a distinct break in the 40° C curve in figure 2 at a solution composition of 14.3 pct HCl and 27.8 pct CoCl₂. This coincided with a jump in the tieline data in figure 4 from a H₂O-CoCl₂ baseline intercept indicating hexahydrate to one indicating tetrahydrate. This coincided with a distinct change in crystal habit from large, red basal tablets to very small, blue-violet elongated prisms.

A further transition from the tetrahydrate to the dihydrate is indicated in figure 4 at a solution composition of 17.7 pct HCl and 23.8 pct CoCl₂, but no corresponding invariant point is apparent in figure 2. Since the tieline data are not as accurate as the solution composition data, additional experimentation is needed to prove or disprove the existence of a CoCl₂·4H₂O phase. The aqueous solubility data in Linke-Seidell show a narrow temperature region from 49° to 58° C in which a CoCl₂·4H₂O solid phase can exist, but other researchers do not support the formation of this phase (3-4, 12). Minimum CoCl₂ solubility occurred at 23.9 pct HCl and was 19.6 pct CoCl₂. A slight increase to 21.6 pct CoCl₂ solubility was observed at HCl saturation of 28.4 pct.

Cobalt chloride concentration and specific gravity as functions of HCl concentration at 60° C are tabulated in table A-3 and plotted in figures 2 and 5. The solubility curve in figure 2 is parallel to the 20° and 40° C curves, starts at an aqueous solubility of 48.3 pct CoCl₂, and decreases in CoCl₂ concentration at a slope of -1.3 pct CoCl₂ per percent HCl to a minimum at 23.0 pct HCl and 24.0 pct CoCl₂. A CoCl₂ concentration of 24.2 pct is obtained at HCl saturation of 24.4 pct. Data in Linke-Seidell show 48.4 pct CoCl₂ solubility at 60° C and a solid phase of CoCl₂·2H₂O. Blue, elongated prisms were noted throughout the experiment. There were no breaks in the solubility curve, and the tieline data in figure 5 indicate a CoCl₂·2H₂O composition. When data from the above

FIGURE 4. - Tieline plot of the data for the CoCl₂-HCl-H₂O system at 40° C.
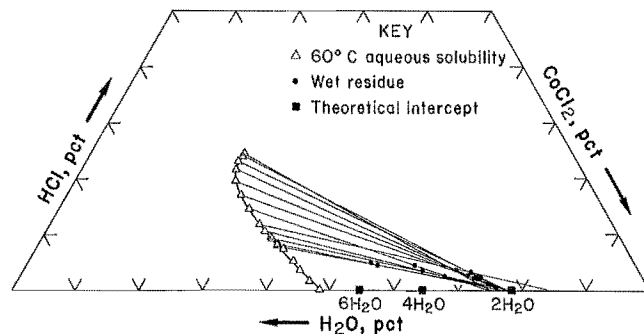
FIGURE 5. - Tieline plot of the data for the CoCl₂-HCl-H₂O system at 60° C.

experiments at 20°, 40°, and 60° C and for 0° and 25° C from Linke-Seidell are plotted as a family of curves, the curves are approximately parallel, with corresponding points, such as minimums and invariants, lying above and to the left as the temperature is increased.

MANGANESE CHLORIDE

$MnCl_2$ concentration and specific gravity as functions of HCl concentration at 20° C are tabulated in table A-4 and plotted in figures 6 and 7. The 20° C curve in figure 6 indicates a solubility ranging from saturation at 42.6 pct $MnCl_2$ in water (compared to 42.5 pct in Linke-Seidell), to 15.2 pct $MnCl_2$ at 23.0 pct HCl, to an invariant point at 16.3 pct $MnCl_2$-25.2 pct HCl concentration, to a minimum of 11.3 pct $MnCl_2$ at 33.7 pct HCl, and to 11.9 pct at HCl saturation of 35.0 pct. The steepest portion of the curve has a slope of -1.4 pct $MnCl_2$ per percent HCl. The sharp break in the curve is an invariant point marking the transition from $MnCl_2 \cdot 4H_2O$ to $MnCl_2 \cdot 2H_2O$. This conclusion is supported by the tielines in figure 7 and by the observation of a change from fairly large, pink, basal tablets to very fine, pink elongated prisms. The solubility and solid phase data agree with those from equilibrium tests made by Balarew (6) at 25° C that show almost parallel, but slightly higher, curves with an invariant point at 18.3 pct $MnCl_2$-22.7 pct HCl, and wet residue tieline plots indicating the transition from $MnCl_2 \cdot 4H_2O$ to $MnCl_2 \cdot 2H_2O$. The aqueous solubility information in Linke-Seidell shows a solid-phase transition from tetrahydrate to anhydrous at 60° C, whereas thermal decomposition data in Colton and Canterford (12) indicate the following transitions:
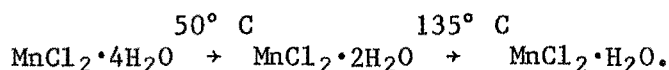
$$MnCl_2 \cdot 4H_2O \xrightarrow{50° C} MnCl_2 \cdot 2H_2O \xrightarrow{135° C} MnCl_2 \cdot H_2O.$$

$MnCl_2$ concentration and specific gravity as functions of HCl concentration at 40° C are tabulated in table A-5 and plotted in figures 6 and 8. $MnCl_2$ solubility was 46.7 pct compared to 47.0 pct in Linke-Seidell. Crystallization by

sparging with HCl decreased the solubility of $MnCl_2$ to a minimum of 14.4 pct at HCl saturation of 30.9 pct. The initial slope of -1.4 pct $MnCl_2$ per percent HCl was parallel to the 20° and 60° C curves. There was a possible small inflection point at 28.2 pct $MnCl_2$-15.8 pct HCl that marked the transition from $MnCl_2 \cdot 4H_2O$ to $MnCl_2 \cdot 2H_2O$ in the salted-out crystals. Tieline data in figure 8 show the breakpoint at the same place. Visual

FIGURE 6. - Solubility of $MnCl_2$ as functions of HCl concentration and temperature in the system $MnCl_2$-HCl-H_2O.
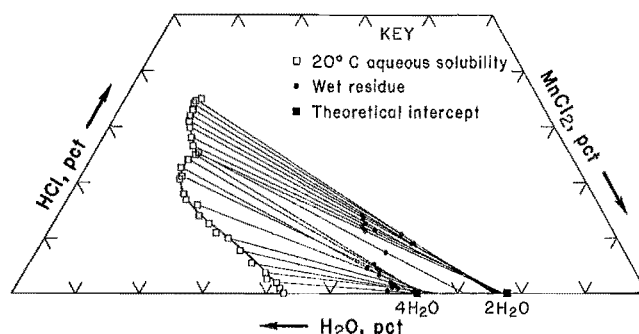
FIGURE 7. - Tieline plot of the data for the $MnCl_2$-HCl-H_2O system at 20° C.
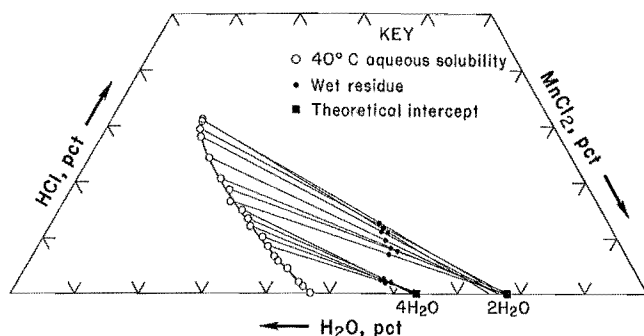
FIGURE 8. - Tieline plot of the data for the $MnCl_2$-HCl-H_2O system at 40° C.

FIGURE 9. - Tieline plot of the data for the $MnCl_2$-HCl-H_2O system at 60° C.

observation also showed a change from large basal tablets to very fine elongated prisms. This experiment was compared with conventional equilibrium experimentation at 40° C by Balarew (6). The agreement in the two sets of data was within 0.5 pct. Balarew found that the transition from tetrahydrate to dihydrate was at 29.1 pct $MnCl_2$-16.2 pct HCl. HCl saturation was determined to be 30.9 pct, compared with 25.3 pct by Balarew.

$MnCl_2$ concentration and specific gravity as functions of HCl concentration at 60° C are tabulated in table A-6 and plotted in figures 6 and 9. The 60° C curve starts with aqueous solubility of 52.1 pct (same value as in Linke-Seidell). The 60° C curve has no breaks and slopes at -1.4 pct $MnCl_2$ per percent HCl. The tieline data in figure 9 show a single convergence at a composition of $MnCl_2 \cdot 2H_2O$. Microscopic examination of the crystals showed very small elongated prisms, which were expected because decomposition data in Colton and Canterford indicated that the solid phase at 60° C was dihydrate. Linke-Seidell found anhydrous $MnCl_2$ at 60° C and a transition to dihydrate at 146° C; these conditions are not likely. The minimum $MnCl_2$ solubility occurred at $MnCl_2$ concentration of 19.5 pct and HCl saturation of 25.5 pct.

NICKEL CHLORIDE

Data for the system $NiCl_2$-HCl-H_2O at 20° C were tabulated in table A-7 and plotted in figures 10 and 11. Solubility of $NiCl_2$ ranged from 37.7 pct in water to
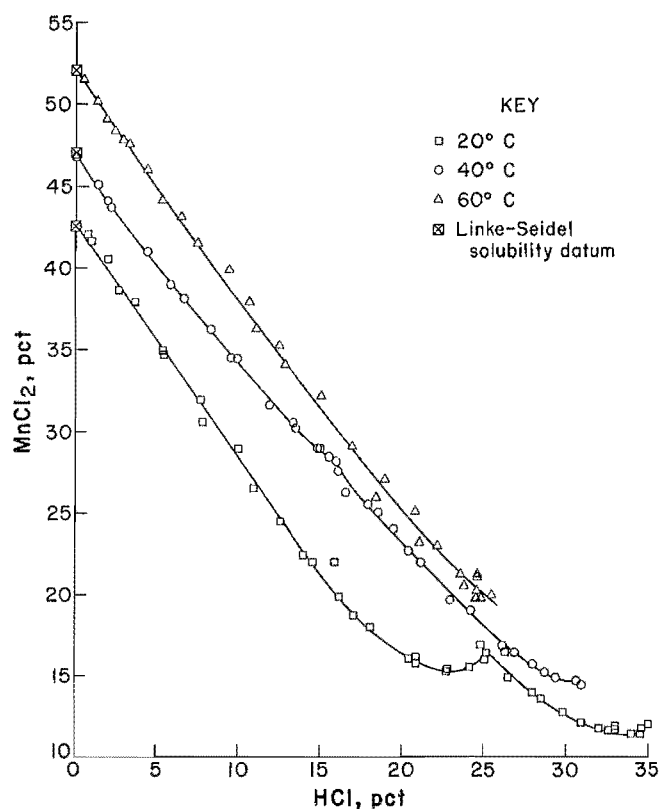

FIGURE 10. - Solubility of $NiCl_2$ as functions of HCl concentration and temperature in the system $NiCl_2$-HCl-H_2O.
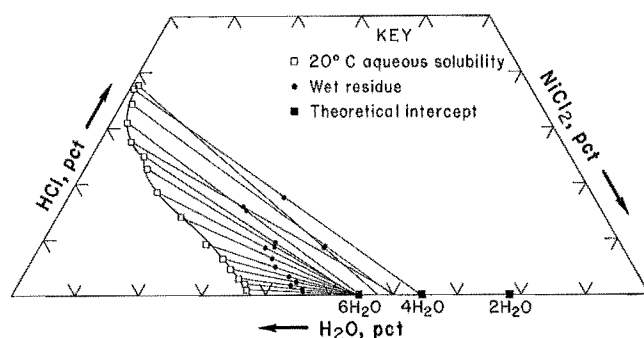
FIGURE 11. - Tieline plot of the data for the $NiCl_2$-HCl-H_2O system at 20° C.
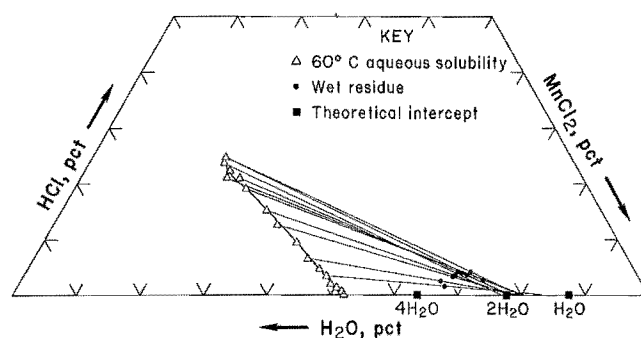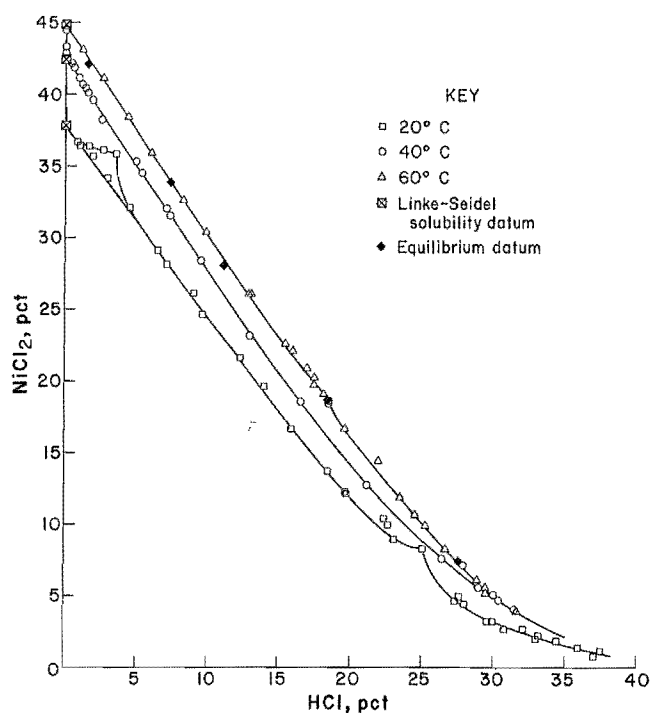
0.7 pct in 37.1 pct HCl and 1.1 pct at HCl saturation of 37.5 pct. The slope of the curve is -1.3 pct $NiCl_2$ per percent HCl and is approximately parallel to that of the 40° and 60° C curves. Breakpoints in the solubility curve occur at $NiCl_2$ and HCl concentrations of 35.8 pct and 3.6 pct, 8.2 pct and 25.1 pct, and 1.3 pct and 36.0 pct, respectively. The first break in the curve was observed in one experiment but not in another and was not caused by a phase change, because up to solution composition of 8.2 pct $NiCl_2$-25.1 pct HCl, the tielines in figure 11 coverage on a $NiCl_2 \cdot 6H_2O$ composition. The crystals were large, green basal tablets characteristic of the hexahydrate. Babaeva and Archakova (5) performed equilibrium tests on this system at 20° C, and Balarew (6) performed equilibrium tests at 25° C. Babaeva and Archakova observed no breakpoint, and their curve coincided with the curve in figure 10, in which a break was not obtained. Data of Balarew showed a breakpoint at about the same point as shown in figure 10. A metastable state must be occasionally formed in sparging and equilibrium tests.

The second break in the curve was noted at 8.2 pct $NiCl_2$-25.1 pct HCl, whereas Babaeva and Archakova found the break at 11.6 pct $NiCl_2$-21.2 pct HCl and Balarew found the break at between 20.42 pct $NiCl_2$-13.71 pct HCl and 20.17 pct $NiCl_2$-14.46 pct HCl. The data of Babaeva and Archakova are in approximate agreement with figure 10, while the data of Balarew show a break at higher $NiCl_2$ and lower HCl concentration, as would be expected for a higher temperature. Both groups of researchers attributed the break to the invariant point corresponding to the phase change from $NiCl_2 \cdot 6H_2O$ to $NiCl_2 \cdot 4H_2O$. The tieline data in figure 11 do not show a clear-cut transition. A change of phase is indicated at 8.2 pct $NiCl_2$-25.1 pct HCl, but the tieline

intersection is not precise and the location is intermediate to the hexahydrate and tetrahydrates. Microscopic examination showed that the crystals were green, basal tablets with a very large 2V and an index of refraction slightly less than 1.600 and verified that the crystals precipitated in 0 to 25.1 pct HCl concentration were the hexahydrate. The crystals produced at HCl concentrations greater than 25.1 pct were yellow-green, more platey than prismatic, but not well defined. The crystals had a 2V+ of 45 to 52 and an index of refraction of 1.600. Therefore, it is likely that the breakpoint at 25.1 pct HCl concentration represents the phase transition of $NiCl_2 \cdot 6H_2O$ to $NiCl_2 \cdot 4H_2O$.

The crystals obtained at 1.1 pct $NiCl_2$-37.5 pct HCl concentrations were orthorhombic, elongated prisms, yellow, very small, and difficult to filter, and had indices of refraction slightly greater than 1.600. These crystals were probably dihydrate, even though the tieline data showed that the composition was tetrahydrate, and there were no obvious breaks in the solubility curve. Babaeva and Archakova did not observe a tetrahydrate-to-dihydrate transition because the maximum HCl concentration was 30.7 pct. Balarew found a tetrahydrate-to-dihydrate phase change at 25° C, 4.0 pct $NiCl_2$, and 29.6 pct HCl. The transition occurred at a HCl concentration of 6 to 8 pct less than noted in this work and is reasonable because of the 5° C temperature difference.

More research needs to be done on the $NiCl_2$-HCl-H_2O system to resolve experimental uncertainties and to reconcile contradictions in the literature. The aqueous solubility data in Linke-Seidell show

$$NiCl_2 \cdot 6H_2O \xrightarrow{28.8° C} NiCl_2 \cdot 4H_2O \xrightarrow{64.3° C} NiCl_2 \cdot 2H_2O,$$
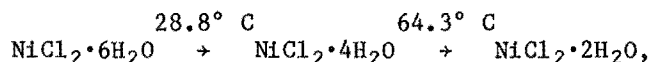
while the data of Babaeva and Archakova for 80° C in Linke-Seidell show a solid phase throughout of $NiCl_2 \cdot 4H_2O$. The results of Foote (4) shown in Linke-Seidell that were supposed to be determined at 20° C were actually determined at 0° C and show phase changes from hexahydrate to tetrahydrate at 4.6 pct $NiCl_2$-26.0 pct HCl and from tetrahydrate to dihydrate at 1.4 pct $NiCl_2$-35.0 pct HCl. These are very close to the phase change compositions reported in this paper, even though there was a 20° C temperature difference.

Data for the system $NiCl_2$-HCl-H_2O at 40° C were tabulated in table A-8 and plotted in figures 10 and 12. Solubility in aqueous solution was 43.3 pct, although the best fit to the data points up to 12.5 pct HCl concentration in figure 10 indicates a zero-HCl intercept at 42.4 pct $NiCl_2$. No data for aqueous solubility at 40° C were given in Linke-Seidell, but when data for other temperatures were plotted, the solubility curve intersected the 40° C projection at 42.3 pct $NiCl_2$. Solubility at low HCl concentrations decreased at a slope of -1.5 pct $NiCl_2$ per percent HCl and was almost the same as the 20° and 60° C curves. There were no breaks in the solubility curve. Minimum $NiCl_2$ solubility was 1.0 pct and occurred at HCl saturation of 37.3 pct. The crystals were yellow-green, poorly defined, and more platey than prismatic, and had a 2V+ of 45 to 52 and an index of refraction of 1.600. The tieline data in figure 12 intersect at a point on the baseline corresponding to $NiCl_2 \cdot 4H_2O$ and agree with aqueous solubility data in Linke-Seidell which show a tetrahydrate solid phase at 28.8° to 63.4° C.

Data for the system $NiCl_2$-HCl-H_2O at 60° C were tabulated in table A-9 and plotted in figures 10 and 13. Nickel chloride tetrahydrate salted out of saturated aqueous solution and gave an almost linear solubility curve with a slope of -1.5 pct $NiCl_2$ per percent HCl over the concentration range of 0 to 18.6 pct HCl (44.4 to 18.6 pct $NiCl_2$). Linke-Seidell gives aqueous saturation as 44.8 pct.

A slight break in the solubility curve in figure 10 and a substantial jump in the intersections in the tieline curve in figure 13 show that there is a phase change from $NiCl_2 \cdot 4H_2O$ to $NiCl_2 \cdot 2H_2O$ before the solubility curve decreases to a minimum $NiCl_2$ solubility of 3.8 pct at HCl saturation of 31.7 pct. The phase change from the tetrahydrate to the dihydrate would be expected from the solubility data in Linke-Seidell, which show that there is a phase change from $NiCl_2 \cdot 4H_2O$ to $NiCl_2 \cdot 2H_2O$ at 64.3° C. The crystals changed from poorly defined yellow-green particles to very small, yellow, elongated prisms at the invariant point.

Two lines of evidence show that $NiCl_2$ crystals salted out of solution by HCl sparging are in equilibrium with $NiCl_2$ in solution. The solid diamonds in figure 10 represent solution concentrations of HCl and $NiCl_2$ at 60° C for bottle tests representing equilibrium conditions. The data are very close to the curve constructed with data from sparging experiments. Data from five readings taken 12 to 24 h after cessation of sparging did not differ by more than 0.1 pct from data collected during sparging.

FIGURE 12. - Tieline plot of the data for the $NiCl_2$-HCl-H_2O system at 40° C.
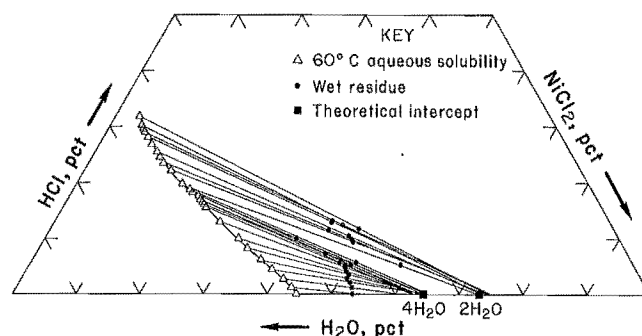
FIGURE 13. - Tieline plot of the data for the $NiCl_2$-HCl-H_2O system at 60° C.

SUMMARY AND CONCLUSIONS

Comparison of published and Bureau data from equilibrium testing showed that HCl sparging experiments gave the same results as equilibrium tests for the $CoCl_2$-, $MnCl_2$-, and $NiCl_2$-HCl-H_2O systems. The chlorides of Co, Mn, and Ni are very soluble in water and have solubilities of 33.9, 42.6, and 37.7 pct, respectively, at 20° C and of 48.3, 52.1, and 44.4 pct, respectively, at 60° C.

Many of the metal chlorides decrease in solubility and salt out of solution owing to the common ion effect when sparged with HCl gas. $NiCl_2$ and $MnCl_2$ fall into this category, although $NiCl_2$ is much less soluble than $MnCl_2$ in solutions saturated with HCl. Some chlorides, such as $FeCl_3$, form strong chloride complexes and become more soluble with HCl addition. $CoCl_2$ is unusual in being very soluble in water and in concentrated HCl and minimally soluble at intermediate HCl concentrations.

The solubility decreases of cobalt, manganese, and nickel chlorides up to HCl concentrations of approximately 15 to 25 pct were linear and approximately parallel, with slopes of -1.3 to -1.5 pct metal chloride per percent HCl. Because of the almost identical behavior and high solubilities, there is little likelihood that the chlorides of cobalt, manganese, or nickel can be separated from one another by sparging to HCl concentrations of less than 15 to 25 pct. At higher HCl concentrations, the solubilities of the three salts diverge owing to large differences in the strengths of the chloride complexes formed. In saturated HCl, the saturation compositions of $CoCl_2$, $MnCl_2$, and $NiCl_2$ were as follows, in percent:

	20° C	40° C	60° C
$CoCl_2$............	18.1	21.6	24.2
$MnCl_2$............	11.9	14.4	19.9
$NiCl_2$............	1.1	1.0	3.8

So it may be possible to separate cobalt and/or manganese from nickel in concentrated HCl. For instance, in the ternary system $CoCl_2$-HCl-H_2O at 20° C, 18 pct $CoCl_2$ will be in solution at 32 pct HCl concentration, whereas in the $NiCl_2$-HCl-H_2O system under comparable conditions, only 2.6 pct $NiCl_2$ will be in solution. Any possible separation scheme must overcome the handling problems inherent with the small elongated prism crystals common to the dihydrate form of the chlorides found at high temperature or in concentrated HCl.

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APPENDIX

TABLE A-1. - $CoCl_2$-HCl-H_2O system at 20° C

Solution			Wet residue		Solution			Wet residue	
HCl, pct	$CoCl_2$, pct	sp gr	HCl, pct	$CoCl_2$, pct	HCl, pct	$CoCl_2$, pct	sp gr	HCl, pct	$CoCl_2$, pct
0.0	33.9	1.38	NA	NA	20.4	9.5	1.17	NA	NA
1.6	31.5	1.36	NA	NA	22.0	9.4	1.17	NA	NA
4.1	28.0	1.33	NA	NA	23.5	10.6	1.20	.3	53.1
6.2	24.9	1.30	0.3	53.0	24.0	12.3	1.23	NA	NA
7.7	22.9	1.28	NA	NA	24.2	15.5	1.25	NA	NA
10.0	20.0	1.26	NA	NA	24.3	16.5	1.28	2.0	50.6
11.2	18.5	1.24	NA	NA	24.3	16.5	1.28	5.9	49.3
12.8	16.6	1.23	NA	NA	24.3	16.5	1.28	10.9	49.0
14.9	14.1	1.21	NA	NA	24.4	16.4	1.27	NA	NA
15.9	12.9	1.20	.5	52.5	26.1	15.8	1.28	NA	NA
16.1	12.8	1.20	NA	NA	27.9	16.0	1.29	8.7	54.4
17.5	11.4	1.19	NA	NA	28.4	16.2	1.29	NA	NA
18.6	10.5	1.18	NA	NA	29.8	17.0	1.31	7.7	54.9
19.7	9.8	1.17	NA	NA	31.9	18.1	1.33	NA	NA

NA Not analyzed.

TABLE A-2. - $CoCl_2$-HCl-H_2O system at 40° C

Solution			Wet residue		Solution			Wet residue	
HCl, pct	$CoCl_2$, pct	sp gr	HCl, pct	$CoCl_2$, pct	HCl, pct	$CoCl_2$, pct	sp gr	HCl, pct	$CoCl_2$, pct
0.0	40.9	1.44	NA	NA	16.6	25.1	1.32	NA	NA
2.0	38.3	1.42	NA	NA	17.1	24.4	1.31	NA	NA
3.8	36.0	1.40	NA	NA	17.5	24.1	1.30	3.0	56.1
4.4	35.3	1.39	NA	NA	17.8	23.8	1.30	9.8	46.9
5.3	34.2	1.38	NA	NA	20.0	21.4	1.27	NA	NA
5.5	33.9	1.38	1.2	49.9	20.6	20.9	1.26	4.5	62.7
7.8	31.4	1.35	1.3	50.5	22.6	19.7	1.25	11.6	46.6
9.5	29.8	1.34	NA	NA	24.1	19.6	1.26	5.9	61.4
11.9	28.1	1.31	1.3	49.4	26.5	20.3	1.29	NA	NA
13.5	27.7	1.33	NA	NA	26.9	20.7	1.29	7.2	58.4
14.3	27.8	1.35	2.1	49.7	27.8	21.2	1.31	4.4	64.3
14.5	27.5	1.35	NA	NA	28.4	21.6	1.31	NA	NA
15.1	26.8	1.34	3.6	54.1					

NA Not analyzed.

TABLE A-3. - $CoCl_2$-HCl-H_2O system at 60° C

Solution			Wet residue		Solution			Wet residue	
HCl, pct	$CoCl_2$, pct	sp gr	HCl, pct	$CoCl_2$, pct	HCl, pct	$CoCl_2$, pct	sp gr	HCl, pct	$CoCl_2$, pct
0.0	48.3	1.58	NA	NA	14.4	30.0	1.36	4.3	61.0
1.6	46.0	1.55	NA	NA	14.5	30.2	1.36	NA	NA
3.6	43.5	1.52	NA	NA	16.9	27.4	1.33	2.4	70.4
5.3	41.6	1.49	NA	NA	17.3	27.3	1.33	NA	NA
7.3	39.0	1.46	NA	NA	19.6	25.2	1.31	1.9	71.7
7.4[1]	39.0	NA	NA	NA	21.7	24.3	1.30	3.3	68.1
7.9	37.7	1.45	4.3	55.2	23.0	24.0	1.31	2.0	72.7
8.2	37.6	1.44	4.7	54.0	23.0[1]	24.3	NA	NA	NA
9.2	36.2	1.43	2.3	66.8	23.9	24.2	1.32	2.9	70.2
9.5	36.0	1.42	NA	NA	23.9	24.2	1.32	2.1	73.5
10.5	34.5	1.41	3.4	62.7	24.0	24.3	1.32	2.5	70.1
11.7	33.5	1.39	NA	NA	24.1	24.2	1.32	2.6	71.1
11.8	33.0	1.39	3.2	70.3	24.4	24.2	1.33	3.6	68.1

NA Not analyzed.
[1]Reading from solution after stirring at temperature for at least 12 h with no sparging.

TABLE A-4. - $MNCl_2$-HCl-H_2O system at 20° C

Solution			Wet residue		Solution			Wet residue	
HCl, pct	$MnCl_2$, pct	sp gr	HCl, pct	$MnCl_2$, pct	HCl, pct	$MnCl_2$, pct	sp gr	HCl, pct	$MnCl_2$, pct
0.0	42.6	1.47	NA	NA	22.7	15.2	1.27	4.6	53.4
.8	42.0	1.46	NA	NA	22.8	15.3	1.27	NA	NA
1.0	41.6	1.46	NA	NA	24.2	15.5	1.28	4.4	55.0
2.1	40.5	1.44	0.7	58.5	24.8	16.8	1.29	NA	NA
2.7	38.6	1.44	NA	NA	25.1	15.9	1.29	5.2	54.2
3.7	37.8	1.43	1.0	59.4	25.2	16.3	1.30	5.1	55.8
5.4	34.8	1.40	1.0	60.2	25.2	16.3	1.30	7.3	54.9
5.4	34.4	1.40	NA	NA	25.3	16.3	1.30	11.2	49.8
7.7	31.8	1.37	1.4	59.4	26.3	15.3	1.29	NA	NA
7.8	30.5	1.37	NA	NA	26.5	14.8	1.29	12.0	48.8
10.0	28.8	1.34	1.8	58.6	28.0	13.9	1.29	11.3	51.2
10.9	26.4	1.33	NA	NA	28.5	13.5	1.28	NA	NA
12.6	24.4	1.31	NA	NA	29.8	12.7	1.28	12.6	49.2
14.0	22.3	1.29	NA	NA	30.9	12.1	1.28	13.5	48.3
14.6	21.9	1.29	NA	NA	32.0	11.7	1.29	13.8	47.9
15.9	20.9	1.27	3.2	56.1	32.6	11.6	1.29	14.1	48.0
16.2	19.8	1.27	NA	NA	33.0	11.8	1.29	NA	NA
17.1	18.6	1.26	NA	NA	33.0	11.6	1.29	8.9	58.2
18.1	17.9	1.26	NA	NA	34.0	11.3	1.29	9.1	58.5
18.2[1]	17.8	1.26	NA	NA	34.6	11.3	1.30	10.8	55.2
20.5	15.9	1.26	NA	NA	34.6	11.3	1.30	10.4	56.2
20.9	16.1	1.26	4.0	55.6	34.7	11.7	1.30	NA	NA
20.9	15.7	1.26	NA	NA	35.0	11.9	1.30	NA	NA

NA Not analyzed.
[1]Reading from solution after stirring at temperature for at least 12 h with no sparging.

TABLE A-5. – $MnCl_2$-HCl-H_2O system at 40° C

Solution			Wet residue		Solution			Wet residue	
HCl, pct	$MnCl_2$, pct	sp gr	HCl, pct	$MnCl_2$, pct	HCl, pct	$MnCl_2$, pct	sp gr	HCl, pct	$MnCl_2$, pct
0.0	46.7	1.53	NA	NA	15.9	28.1	1.36	NA	NA
1.3	45.1	1.51	NA	NA	16.1	27.5	1.36	NA	NA
1.9	44.1	1.50	NA	NA	16.5	26.2	1.36	7.0	55.7
2.2	43.6	1.50	NA	NA	17.9	25.4	1.35	NA	NA
4.4	40.9	1.47	NA	NA	18.5	24.9	1.34	7.5	56.8
5.8	38.8	1.45	NA	NA	19.4	23.9	1.34	NA	NA
6.7	38.0	1.44	NA	NA	20.3	22.6	1.33	8.2	55.3
8.3	36.2	1.42	2.0	57.7	21.1	21.8	1.33	NA	NA
9.5	34.4	1.41	NA	NA	22.9	19.6	1.32	NA	NA
9.4[1]	34.0	1.41	NA	NA	24.2	18.9	1.31	9.3	54.0
9.9	34.3	1.41	2.2	57.3	26.1	16.8	1.30	NA	NA
11.9	31.5	1.39	2.5	56.6	26.8	16.3	1.30	NA	NA
13.3	30.4	1.38	2.1	58.5	27.9	15.6	1.30	10.9	52.6
13.4	30.1	1.38	NA	NA	28.7	15.1	1.29	7.7	59.8
14.8	28.8	1.37	2.6	57.2	29.3	14.8	1.29	11.7	52.4
15.0	28.8	1.37	NA	NA	30.6	14.6	1.29	12.5	51.5
15.5	28.3	1.36	NA	NA	30.9	14.4	1.30	10.8	53.6

NA Not analyzed.
[1]Reading from solution after stirring at temperature for at least 12 h with no sparging.

TABLE A-6. – $MnCl_2$-HCl-H_2O system at 60° C

Solution			Wet residue		Solution			Wet residue	
HCl, pct	$MnCl_2$, pct	sp gr	HCl, pct	$MnCl_2$, pct	HCl, pct	$MnCl_2$, pct	sp gr	HCl, pct	$MnCl_2$, pct
0.0	52.1	1.62	NA	NA	12.8	34.0	1.43	NA	NA
.5	51.5	1.61	NA	NA	15.1	32.1	1.40	3.5	67.8
1.3	50.2	1.60	NA	NA	16.9	29.0	1.38	NA	NA
1.9	49.1	1.59	NA	NA	18.4	25.8	1.36	NA	NA
2.4	48.3	1.58	NA	NA	18.9	27.0	1.35	2.6	72.6
2.9	47.8	1.57	NA	NA	20.8	25.0	1.34	4.0	67.9
3.3	47.6	1.57	1.6	67.1	21.1	23.1	1.33	3.6	69.7
3.3[1]	47.9	1.57	NA	NA	22.2	22.9	1.32	NA	NA
4.4	46.0	1.55	NA	NA	23.6	21.2	1.32	3.6	68.1
5.3	44.1	1.54	NA	NA	23.8	20.5	1.32	NA	NA
6.5	43.1	1.52	2.5	66.1	24.5	19.7	1.32	NA	NA
7.5	41.4	1.51	NA	NA	24.6	20.1	1.32	NA	NA
9.4	39.8	1.48	NA	NA	24.6	21.2	1.32	4.0	68.6
10.7	37.8	1.46	NA	NA	24.6	21.0	1.32	4.1	70.0
11.1	36.2	1.46	NA	NA	24.8	19.7	1.33	NA	NA
12.5	35.2	1.44	3.2	67.5	25.5	19.9	1.33	NA	NA

NA Not analyzed.
[1]Reading from solution after stirring at temperature for at least 12 h with no sparging.

TABLE A-7. - $NiCl_2$-HCl-H_2O system at 20° C

Solution			Wet residue		Solution			Wet residue	
HCl, pct	$NiCl_2$, pct	sp gr	HCl, pct	$NiCl_2$, pct	HCl, pct	$NiCl_2$, pct	sp gr	HCl, pct	$NiCl_2$, pct
0.0	37.7	1.49	NA	NA	22.4	10.3	1.21	NA	NA
.8	36.7	1.48	NA	NA	22.7	9.8	1.21	8.4	37.2
1.0	36.3	1.47	0.7	45.3	23.1	8.9	1.21	NA	NA
1.7	36.3	1.46	NA	NA	25.1	8.2	1.19	9.0	.36.8
1.9	35.7	1.46	.9	45.2	27.3	4.6	1.18	NA	NA
2.7	36.1	1.44	NA	NA	27.6	4.9	1.18	15.8	28.3
2.7[1]	36.1	NA	NA	NA	28.0	4.4	1.17	NA	NA
3.0	34.2	1.44	1.6	43.1	29.6	3.2	1.17	NA	NA
3.6	35.8	1.43	NA	NA	30.0	3.2	1.16	NA	NA
4.6	32.1	1.42	2.3	43.5	30.8	2.7	1.17	15.0	29.3
6.6	29.1	1.39	3.2	41.9	32.1	2.6	1.17	NA	NA
7.2	28.1	1.38	NA	NA	33.0	1.9	1.18	NA	NA
9.1	26.1	1.35	4.9	38.9	33.2	2.2	1.18	NA	NA
9.7	24.6	1.34	NA	NA	34.3	1.7	1.18	8.7	44.9
12.3	21.6	1.30	NA	NA	35.8	1.6	1.19	NA	NA
14.0	19.6	1.28	6.5	37.7	36.0	1.3	1.19	NA	NA
15.9	16.6	1.26	NA	NA	37.1	.7	1.19	17.5	34.1
18.5	13.7	1.24	8.5	35.6	37.5	1.1	1.20	8.3	44.7
19.7	12.2	1.23	NA	NA					

NA Not analyzed.

[1]Reading from solution after stirring at temperature for at least 12 h with no sparging.

TABLE A-8. - $NiCl_2$-HCl-H_2O system at 40° C

Solution			Wet residue		Solution			Wet residue	
HCl, pct	$NiCl_2$, pct	sp gr	HCl, pct	$NiCl_2$, pct	HCl, pct	$NiCl_2$, pct	sp gr	HCl, pct	$NiCl_2$, pct
0.0	43.3	1.53	NA	NA	7.3	31.5	1.41	2.3	55.1
.4	42.2	1.52	NA	NA	9.6	28.3	1.38	3.4	52.8
.6	41.8	1.52	NA	NA	13.0	23.1	1.32	4.0	52.5
.9	41.1	1.52	NA	NA	16.6	18.5	1.29	5.2	51.6
1.2	40.7	1.51	NA	NA	16.7[1]	18.3	1.28	NA	NA
1.4	40.4	1.51	NA	NA	21.2	12.7	1.25	6.2	49.9
1.6	40.1	1.51	NA	NA	26.4	7.5	1.20	7.2	49.1
1.9	39.6	1.50	NA	NA	29.0	5.5	1.19	NA	NA
2.6	38.2	1.49	NA	NA	30.1	5.0	1.18	7.9	49.4
5.0	35.3	1.45	1.9	53.6	30.4	4.7	1.18	NA	NA
5.4	34.5	1.44	1.9	53.8	31.5	4.0	1.18	NA	NA
7.2	32.0	1.41	2.6	53.7	37.3	1.0	1.17	NA	NA

NA Not analyzed.

[1]Reading from solution after stirring at temperature for at least 12 h with no sparging.

TABLE A-9. - $NiCl_2$-HCl-H_2O system at 60° C

Solution			Wet residue		Solution			Wet residue	
HCl, pct	$NiCl_2$, pct	sp gr	HCl, pct	$NiCl_2$, pct	HCl, pct	$NiCl_2$, pct	sp gr	HCl, pct	$NiCl_2$, pct
0.0	44.4	1.56	NA	NA	22.0	13.8	1.24	9.4	48.7
1.2	43.1	1.55	0.0	53.2	21.8[1]	13.9	1.26	NA	NA
2.7	41.1	1.52	1.2	52.6	23.5	11.8	1.24	9.7	48.4
4.4	38.4	1.49	2.1	51.8	24.6	10.6	1.23	NA	NA
6.1	35.8	1.47	2.7	51.2	25.3	9.8	1.23	10.4	47.5
8.3	32.6	1.43	3.3	51.1	26.7	8.2	1.21	NA	NA
8.2[1]	32.6	1.43	NA	NA	26.4[1]	8.3	1.21	NA	NA
9.9	30.3	1.40	4.0	50.3	27.9	7.0	1.20	12.8	43.4
12.9	26.0	1.35	4.7	49.8	28.9	6.0	1.20	NA	NA
13.1	26.0	1.35	4.9	49.6	28.9	6.1	1.20	12.3	45.5
15.5	22.5	1.32	5.6	48.5	29.5	5.5	1.19	12.5	43.8
15.6[1]	22.5	1.32	NA	NA	29.9	5.1	1.19	13.0	43.5
16.0	22.0	1.32	7.2	45.3	31.7	3.8	1.19	11.6	48.4
16.0[1]	21.8	1.32	NA	NA	EQUILIBRIUM DATA FROM CLOSED-VESSEL				
17.0	20.8	1.31	5.1	50.3	EXPERIMENTS				
17.5	19.7	1.30	9.8	39.5	0.0	44.3	1.56	NA	NA
17.5	20.2	1.30	6.3	47.2	1.6	42.1	1.54	0.9	49.6
18.2	19.0	1.29	4.9	51.1	7.4	33.8	1.44	3.9	46.9
18.6	18.3	1.29	5.7	49.5	11.2	28.0	1.38	3.6	51.6
18.6	18.5	1.29	5.6	51.1	18.4	18.6	1.29	5.1	58.2
19.7	16.6	1.28	NA	NA	27.6	7.3	1.20	6.5	58.8

NA Not analyzed.

[1]Reading from solution after stirring at temperature for at least 12 h with no sparging.